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U.S. PATENT APPLICATION

for

LITHIUM BASED ELECTROCHEMICAL CELL SYSTEMS

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[0001] This application claims priority to United States Provisional Patent Application No. 60/434,214, filed on December 17, 2002 and incorporated herein by reference.

[0002] This invention was made with government support under Contract No. W-31-109-ENG-38 awarded to the Department of Energy. The Government has certain rights in this invention.

BACKGROUND OF THE INVENTION

[0003] Gas generation in both Li-ion and lithium-metal based primary and secondary electrochemical cells may become a serious problem both during normal cell operation at room temperature and, more especially, at elevated temperatures. The consequence of gas build up includes cell can expansion and subsequent can rupture, leading to cell and or battery failure. For example, the gassing problem has been observed to be extremely serious in large electric vehicle type cell systems and in pouch type cell systems where rupture of the cell containment leads to serious safety problems. The gassing problem is also very serious in lithium-metal based primary cells using liquid and/or solid electrolytes *in vivo* applications such as for heart pacemakers and similar devices.

[0004] Because both the negative and positive electrodes in the charged states of nearly all lithium based electrochemical cell systems are thermodynamically unstable in respect to the electrolyte, it is especially important that electrolyte additives be developed to stabilize the electrodes

by decreasing the kinetics of the respective electrode reactions and thereby reducing the gas generation.

SUMMARY OF THE INVENTION

[0005] This invention is directed toward the development of both primary and secondary Li-ion and lithium-metal based electrochemical cell systems in which the suppression of gas generation is achieved through the addition of an additive or additives to the electrolyte system of the respective cell, or to the cell whether it be a liquid, a solid- or plastized polymer electrolyte system. The gas suppression additives in this patent application are primarily based on unsaturated hydrocarbons and nitrogen containing organic materials.

BRIEF DESCRIPTION OF THE DRAWINGS

[0006] Figure 1 shows cycle life characteristics of a Li-ion cell (ANL- 1) containing 1.0 wt% 2,3 dimethyl-1,3 butadiene with the 1 M $LiPF_6$ dissolved in ethylene carbonate (30%) and ethyl-methyl carbonate (70%);

[0007] Figure 2 shows cycle life characteristics of a Li-ion cell(ANL-2) containing 2.0 wt% VEC and 1.0wt% 2,3 dimethyl-1,3 butadiene with the 1 M LiPF6 dissolved in ethylene carbonate(20%), propylene carbonate(20%), and diethyl carbonate(60%); and

[0008] Figure 3 shows changes of gas pressure change during ARC measurements of negative electrodes and electrolytes from Li-ion (ANL-1) cells with additives and a reference cell negative electrode and electrolyte from a (ANL-1) cell, but without additives.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0009] By use of appropriate additive or additives, the primary and secondary electrochemical Li-ion cells of this invention have minimal gassing and possess high specific energy and power, as well as excellent calendar and cycle life across a broad temperature range. The additives that are capable of ameliorating gas generation in the lithium based electrochemical cells include at least the following class of organic compounds, which will be described in more detail hereinafter: (a) $CH_2=R_1=CH_2$, where R_1 is an aliphatic carbon chain of 1 to 7 carbons, either linear or branched (b) $CH\equiv R_1\equiv CH$, (c) $CH_2=R_1$, (d) $CH\equiv R_1$, (e) $R_2\text{-}CH=R_1=CH_2$, where R_2 is an aromatic (toluene or benzene), a cyclic hydrocarbon, (f) $R_2\text{-}C\equiv R_1\equiv CH$, (g) $R_2\text{-}CH=R_1$, (h) $R_2\text{-}C\equiv R_1$, (i) styrene carbonate, (j) aromatic carbonates, (k) vinyl pyrrole, (l) vinyl piperazine, (m) vinyl piperidine, (n) vinyl pyridine, (o) triphenyl phosphate and blends thereof. These blends may involve other additives such as vinyl ethylene carbonate to protect against exfoliation in propylene carbonate based Li-ion electrolyte systems.

[0010] The present invention provides electrochemical lithium-based primary and secondary cells with excellent calendar life across a broad temperature, and includes cells with liquid and solid- and plastized polymer electrolytes.

[0011] Figure 1 shows the improved cycle life characteristics of a Li-ion cell (ANL-1) containing l.0 wt% 2,3 dimethyl-1,3 butadiene (DMB). The cell utilized a crystalline graphite anode, a $LiNi_{0.8}Co_{0.2}O_2$ cathode and an electrolyte containing 1 M $LiPF_6$ dissolved in a blend of ethylene carbonate and ethyl-methyl carbonate.

[0012] Figure 2 shows the improved cycle life characteristics of a Li-ion cell (ANL-2) containing 2.0 wt% VEC and 1.0 wt% 2,3 dimethyl-1,3

butadiene with the 1 M $LiPF_6$ dissolved in blend of ethylene carbonate, propylene carbonate, and dimethyl carbonate. The cell utilized the same cathode and anode as cell (ANL-1).

[0013] Figure 3 shows the gas pressures developed by studies of the respective negative electrodes with electrolyte from cell (ANL-1) and compares the pressures developed by the negative electrodes and electrolyte from a similar cell that did not contain the 2,3 dimethyl-1,3 butadiene. The results of these studies indicate the additives significantly reduce the degree of gassing in the negative electrodes of cell (ANL-1), as compared to the negative electrode/electrolyte gassing from a similar cell but without the additive package. The additive effects in reducing pressure buildup are especially effective with the negative electrodes. The additives were also found to increase the activation energy and decrease the heat of reaction around the onset temperature that is believed to be the onset temperature for thermal runaway in the commercial lithium ion cells. The result of these studies indicate that these additives may be very effective in reducing gas buildup in high energy lithium-based cells for many different applications such as electric and hybrid vehicles, as well as *in vivo* applications such as for heart pacemakers and other implantable devices for the human body.

[0014] According to one embodiment of the invention, lithium electrochemical cell systems include:

[0015] (i) A secondary Li-ion cell comprising a lithium metal oxide positive electrode, a negative electrode containing a crystalline carbon like graphite, an electrolyte composed of a lithium salt, and a blend of at least two aprotic solvents. The solvents include ethylene carbonate, dimethyl carbonate, ethyl methyl carbonate, propylene carbonate, or diethyl carbonate, and finally a compound that reduces cell gassing. The salts

include $LiPF_6$, $LiBF_4$, $LiAsF_6$, and other salts currently being used or being developed such as the lithium bisoxlatoborate (LiBOB) salts.

[0016] (ii) A Li-ion secondary electrochemical cell similar to the cell type (i) described above except that the electrolyte is either a liquid gel or solid polymer with a dissolved salt such as $LiClO_4$, $LiPF_6$, $LiBF_4$, $LiAsF_6$, $LiCF_3SO_3$, $Li(CF_3SO_2)_2N$, $Li(CF_3SO_2)_3C$, $LiN(SO_2C_2F_5)_2$, lithium alkyl fuorophosphate, lithium bis(chelato)borates and mixtures thereof; or a solid polymer blended with the electrolyte described above in cell type (i), called a plastized electrolyte. These electrolytes also contain a degassing agent.

[0017] (iii) A lithium-metal based primary or secondary electrochemical cell. This cell is similar to those described above except that they use lithium metal as the negative electrode, a metal oxide positive electrode such as $LiCoO_2$, $LiNiO_2$, $LiNi_{1-x}Co_yMe_zO_2$, $LiMn_{0.5}Ni_{0.5}O_2$, $LiMn_{0.3}Co_{0.3}Ni_{0.3}O_2$, $LiFePO_4$, $LiMn_2O_4$, $LiFeO_2$, $LiMc_{0.5}Mn_{1.5}O_4$, vanadium oxide, and mixtures thereof, wherein Me is Al, Mg, Ti, B, Ga, or Si, and Mc is a divalent metal such as Fe, Co, Cu, Cr and Ni, and either a liquid electrolyte described in (i) liquid or solid polymer or plastized electrolyte described in cell types (ii) above and that contains a degassing agent.

[0018] The agents or additives described herein include the following class of organic compounds; (a) $CH_2=R_1=CH_2$, where R_1 is an aliphatic carbon chain of 1 to 7 carbons, either linear or branched (b) $CH \equiv R_1 \equiv CH$, (c) $CH_2=R_1$, (d) $CH \equiv R_1$, (e) R_2-$C=R_1=CH2$, where R_2 is an aromatic (toluene or benzene), a cyclic hydrocarbon, a pyrrole, a piperazine, or a piperidine molecule, (f) R_2-$C \equiv R_1 \equiv CH$, (g) R_2-$CH=R_1$, (h) R_2-$C \equiv R_1$, (i) styrene carbonate, (j) aromatic carbonates, (k) vinyl pyrrole, (l) vinyl piperazine,(m) vinyl piperidine, (n) vinyl pyridine (o) triphenyl phosphate, (p) and blends thereof. These blends may

involve other additives, such as vinyl ethylene carbonate, to protect against exfoliation in propylene carbonate based Li-ion electrolyte systems.

[0019] The agents or additives described herein can include, for example, 2,3 dimethyl-1,3 butadiene, 1,3 butadiene, is 2,3 dimethyl-1,4 pentadiene, 1,5 hexadiene, a blend of 2,3 dimethyl-1,3 butadiene and vinyl ethylene carbonate, and a blend of 2,3 dimethyl-1,4 pentadiene and vinyl pyridine. Other additives or agents include a blend of 1,5 hexadiene and piperazine, a blend of 2,3 dimethyl-1,3 butadiene and styrene, a blend of 2,3 dimethyl-1,3 butadiene and piperidine, a blend of hexadiene and vinyl pyridine, a blend of 2,3 dimethyl-1,3 butadiene and triphenyl phosphate, a blend of 2,3 dimethyl-1,3 butadiene and vinyl pyridine, styrene carbonate, and a blend of styrene carbonate and vinyl piperazine. Additionally, the additive or agent can also be a blend of two or more of the additives described above. According to one embodiment of the invention, the total concentration of additives ranges from 0.1 to 25 wt%, with an optimum concentration varying from 0.1 to 10 wt%.

[0020] It should be understood that the above description of the invention and the specific examples and embodiments therein, while indicating the preferred embodiments of the present invention, are given only by demonstration and not limitation. Many changes and modifications within the scope of the present invention may therefore be made without departing from the spirit of the invention, and the invention includes all such changes and modifications.